Available at: http://www.ictp.trieste.it/~pub_off IC/2004/68

United Nations Educational Scientific and Cultural Organization
and
International Atomic Energy Agency

THE ABDUS SALAM INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

THE INFLUENCE OF TiO_2 POLYMORPH, MECHANICAL MILLING AND SUBSEQUENT SINTERING ON THE FORMATION OF Ti-SUBSTITUTED SPINEL-RELATED $Li_{0.5}Fe_{2.5}O_4$

H.M. Widatallah[1]
Department of Physics, University of Khartoum, P.O. Box 321, Khartoum 11115, Sudan,
Department of Physics, Sultan Qaboos University, P.O. Box 36, Muscat 123, Oman
and
The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy,

X-L. Ren
Department of Chemistry, Open University, Walton Hall,
Milton Keynes, MK76AA, United Kingdom

and

I.A. Al-Omari
Department of Physics, Sultan Qaboos University, P.O. Box 36, Muscat 123,Oman.

MIRAMARE – TRIESTE

August 2004

[1] Regular Associate of the Abdus Salam ICTP.
Corresponding author. hisham@ictp.trieste.it, hishamm@squ.edu.om

Abstract

Single-phased spinel-related titanium-substituted $Li_{0.5}Fe_{2.5}O_4$ has been synthesized by sintering in air a mechanically pre-milled mixture of lithium carbonate, corundum-related iron (III) oxide and the rutile polymorph of titanium (IV) oxide at 700ºC (12h). This temperature is *ca.* 450-500ºC less than the temperatures at which the material is normally prepared by conventional ceramic techniques. On replacing the rutile polymorph of titanium (IV) oxide in the pre-milled mixture by the anatase form the formation of single-phased titanium substituted $Li_{0.5}Fe_{2.5}O_4$ was not achieved even after sintering the mixture at 1000ºC (12h).

1. Introduction

The ferrimagnetic lithium ferrite $Li_{0.5}Fe_{2.5}O_4$ adopts an inverse spinel structure in which all the Li^+ ions and 3/5 of all Fe^{3+} ions occupy the octahedral B-sites whilst the remaining Fe^{3+} ions occupy tetrahedral A-sites [1]. The material is extensively studied due to its desirable electric and magnetic properties that render it attractive in microwave and memory-core applications[1-4]. The magnetic moments on the A- and B-sub-lattices are antiparallel, indicating that the dominant contribution to magnetization comes from the octahedral B-sub-lattice. The magnetic properties of $Li_{0.5}Fe_{2.5}O_4$ can, thus, be modified by substituting magnetic and/or diamagnetic cations for Fe^{3+} ions on either sub-lattice, thus allowing the material to be tailored for a specific application [1]. Ti^{4+}, for instance, is known to have a strong octahedral site preference and therefore works very well for magnetization reduction [1]. The incorporation of Ti^{4+} in the spinel-related structure of $Li_{0.5}Fe_{2.5}O_4$ is stabilized by excess Li^+ ions above the number in $Li_{0.5}Fe_{2.5}O_4$, that substitute Fe^{3+} on tetrahedral sites, leading to a formula of the type $Li_{0.5+0.5X}Fe_{2.5-1.5x}Ti_xO_4$ [1,5,6]. Normally, the material is prepared by the conventional ceramic double sintering method in which solid state reactions between oxides and/or carbonates of Li, Fe(III) and Ti(IV) require prolonged heat exposure at elevated temperatures (typically ~1200ºC) [1,7,8]. One of the disadvantages of high temperature sintering is the volatility of Li_2O and the irreversible reduction of Fe^{3+} to Fe^{2+} with the consequent precipitation of α-Fe_2O_3 and Fe_3O_4 depending on the cooling regime adopted [1,4]. As a result, the saturation magnetization of the material is lowered and its conductivity increased limiting its use in, for example, microwave applications where high saturation magnetization and high resistivity are required [1,9]. As a remedy, it has been pointed out that to avoid the drawbacks associated with high temperature-sintering, substituted lithium ferrites should be synthesized at or below 850ºC [10].

We note that although a substantial literature has accumulated on the use of mechanical milling for lowering the temperatures of formation for many ferrites [11], there is only limited information on the use of the technique to synthesize pure or substituted lithium ferrites [4,5,12]. Of particular interest is an earlier investigation [5] which reported the formation of Ti-substituted $Li_{0.5}Fe_{2.5}O_4$ at 870 ºC by milling a mixture of the anatase polymorph of TiO_2, α-Fe_2O_3 and Li_2O followed by double sintering under oxygen flow for 36h. However, the influence of other polymorphs of TiO_2 on the formation of the material was not investigated and the role of the milling process in lowering the material temperature of formation was not identified. It can also be noted that prolonged sintering adopted (36h in total) under oxygen flow makes that preparation route both technically demanding and costly. We report here on a simple method for synthesizing single-phased Ti-substituted $Li_{0.5}Fe_{2.5}O_4$ by sintering in air a pre-milled mixture of α-Fe_2O_3, Li_2CO_3 and the rutile polymorph of TiO_2 at the relatively low temperature of 700ºC for a period 12h. In contrast, we show that sintering a similarly pre-milled mixture, in which the anatase polymorph replaces the rutile form of TiO_2, does not lead to the formation of a single-phased Ti-substituted $Li_{0.5}Fe_{2.5}O_4$ even at 1000ºC (12h). The role of milling in lowering the formation temperature is stressed.

2. Experimental

To prepare Ti-substituted $Li_{0.5}Fe_{2.5}O_4$ of the composition $Li_{0.65}Fe_{2.05}Ti_{0.3}O_4$ (*i.e.* x= 3 in the general formula $Li_{0.5+0.5X}Fe_{2.5-1.5x}Ti_xO_4$), the corresponding molar amounts of TiO_2 (in either the anatase or rutile form), α-Fe_2O_3 and Li_2CO_3 were well mixed and dry-milled in a Retsch PM400 planetary ball mill with a stainless steel vial (250 ml) and balls (20mm) operating at a milling speed of

200 rpm for 190 hours. The powder to ball weight ratio was 1:20. Small amounts of milled powders were removed at intervals during the milling. The milled powder was then sintered for 12-h periods in air at temperatures between 300ºC and 1000ºC. Following each heat-treatment the material is quenched in air. X-ray powder diffraction patterns were recorded with a Siemens D5000 diffractometer using CuKα radiation. The program powdercell was used to analyze the X-ray powder diffraction [13]. ^{57}Fe Mössbauer measurement was recorded at room temperature using a microprocessor-controlled Mössbauer spectrometer with a 25 mCi ^{57}Co/Ph source. Chemical isomer shift data are quoted relative to that of metallic iron at room temperature.

3. Results and Discussion

3.1.a Milling the rutile-containing mixture

The X-ray powder diffraction patterns recorded from the mixture of α-Fe_2O_3, Li_2CO_3 and the rutile polymorph of TiO_2 following mechanical milling in air for various periods of time are collected in Fig. 1.

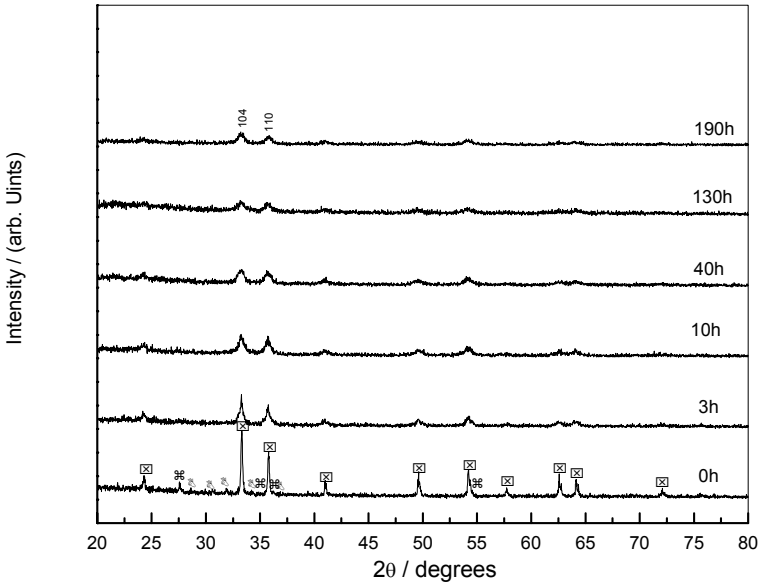

Fig.1: X-ray powder diffraction patterns recorded from the mixture of α-Fe_2O_3 (ξ), rutile modification of TiO_2 (ζ) and Li_2CO_3 (B) following ball milling at the times indicated. 110 and 104 are the Miller indices of the α-Fe_2O_3 reflection peaks shown indicated.

The X-ray powder diffraction pattern of the non-milled (0h) mixture shows the peaks characteristic of the initial reactants. The very low peak-intensities of the rutile and Li_2CO_3 components relative to those of α-Fe_2O_3 reflects both their small quantities as well as the low scattering factors of both Ti^{4+} and Li^+ relative to that of Fe^{3+}[5]. After milling for 3h, the peaks corresponding to Li_2CO_3 and rutileTiO_2 almost disappear, while those attributable to α-Fe_2O_3 start to broaden and decrease in intensity indicating a significant decrease in the crystallite size for all components. Milling the mixture for periods between 10h and 190h shows a gradual broadening and intensity decrease of the reflection peaks of the α-Fe_2O_3 related phase. The variation of the crystallite

size of this phase, determined from the X-ray diffraction data using the Scherrer formula, versus milling time is shown in Fig. 2. While a fast decrease in the crystallite size is observed in the first 10h of milling from *ca.* 1.1 μm to *ca.* 17nm , for the next 180h only a slight decrease is observed.

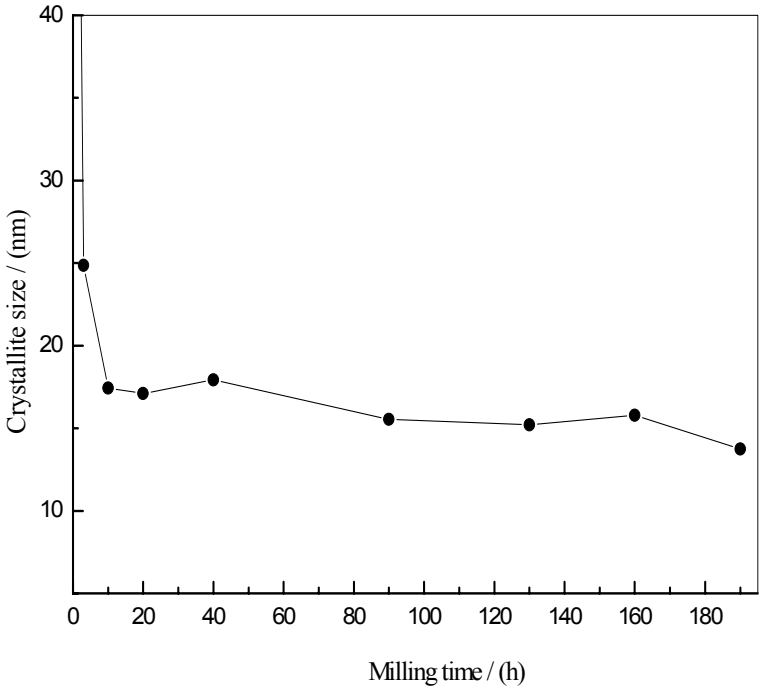

Fig. 2: Variation of the crystallite size with milling time for the α-Fe_2O_3 related phase for the mixture of α-Fe_2O_3, rutile modification of TiO_2 and Li_2CO_3.

It is interesting to note that with increasing milling time, the intensity of the 104 reflection peak of the α-Fe_2O_3-related phase (at *ca.* 33° 2θ) (Fig. 1) decreases relative to that of the 110 peak (at *ca.* 36° 2θ) until both peaks become approximately equal in intensity. A similar behavior was reported when Li^+ [4] or Ti^{4+} [14] were incorporated in the α-Fe_2O_3 structure. This is suggestive that milling induces a reaction between the reactants to form Li^+- and Ti^{4+}- substituted α-Fe_2O_3 nanoparticles. This is confirmed by comparing the lattice parameters obtained from the α-Fe_2O_3-related phase after milling for 190h with those of pure α-Fe_2O_3. While the variation in the *c* parameter was not significant, the *a* and *b* parameters were found to be 5.027Å relative to 5.035 Å for pure α-Fe_2O_3. We have reported a similar decrease when Li^+ was incorporated in both pure and Ti-substituted α-Fe_2O_3 -related matrix [4,15].

Taken together these results indicate that milling the rutile-containing mixture for 190h induces a reaction that leads to the progressive incorporation of Li^+, Ti^{4+} or both in the nanocrystalline α-Fe_2O_3 structure. Additionally, the absence of reflection peaks attributable Li_2CO_3 and rutile TiO_2 in the X-ray diffraction patterns recorded from samples milled for10h and above can originate from nanoaggregates in which unreacted particles enjoy a large interface and are tightly pressed together.

3.1.b Sintering the pre-milled rutile-containing-mixture

The X-ray powder diffraction patterns recorded from the 190h-milled mixture of α-Fe_2O_3, rutile TiO_2 and Li_2CO_3 following heating at different temperature for 12-h intervals in air are shown in Fig. 3.

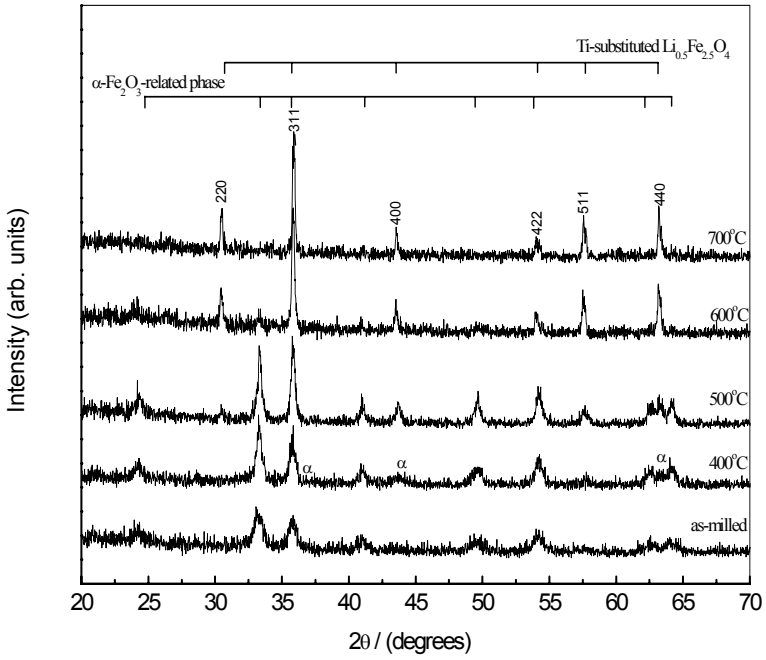

Fig. 3: X-ray powder diffraction patterns recorded from the 190h-pre-milled mixture of α-Fe_2O_3, rutile modification of TiO_2 and Li_2CO_3 following sintering in air for 12-h periods at the temperatures indicated; α refers to α-$LiFeO_2$ related phase.

Sintering the mixture at 400°C (12h) followed by quenching in air resulted in the appearance of very broad peaks of low intensity in the X-ray diffraction indicated by α in Fig. 3. These new peaks are indexed t an α-$LiFeO_2$-related phase (most intense peak is at *ca.* 43.5˚)[16]. A similar phase evolution has been observed when a pre-milled mixture of α-Fe_2O_3 and Li_2CO_3 was submitted to a similar thermal treatment [4]. The enhancement of intensity of the 104 peak relative to that of 110 signifies the removal of Li^+ ions from the α-Fe_2O_3 structure to form the α-$LiFeO_2$-related phase.

When the mixture was sintered at 500°C (12h) and then quenched in air, the peaks corresponding to the α-Fe_2O_3-related phase remain dominant. However a spinel-related $Li_{0.5}Fe_{2.5}O_4$ phase is also formed at this temperature as indicated by the appearance, in Fig. 3, of reflection peaks that could be indexed to it. This is indicative that the α-$LiFeO_2$-related phase is an intermediate one in the formation process of the spinel-related lithium ferrite phase. Sintering of the mixture at 600°C (12h) and then quenching in air shows the X-ray reflection peaks of the α-Fe_2O_3-related phase to nearly disappear while those of the inverse spinel-related $Li_{0.5}Fe_{2.5}O_4$ phase dominate implying that the reaction between the initial components is almost complete.

Further sintering at 700°C (12h) and subsequent quenching in air resulted in the development of a single inverse spinel-related $Li_{0.5}Fe_{2.5}O_4$ phase. To see whether Ti^{4+} ions are

incorporated in the $Li_{0.5}Fe_{2.5}O_4$ structure, we note that only the main spinel reflection peaks originating from the crystalline planes (220), (311), (400), (422), (511) and (440) appear in the pattern. The super-lattice structure peaks that appear in the X-ray diffraction pattern of pure $Li_{0.5}Fe_{2.5}O_4$ at 700°C due to the ordered distribution of Fe^{3+} and Li^{+} over octahedral B-sites are missing. This in turn indicates that the Ti^{4+} ions are incorporated in $Li_{0.5}Fe_{2.5}O_4$ resulting in a random cation distribution over the octahedral B-sites. The value of the lattice parameter *a* obtained is 0.833 nm which is nearly the same as that of pure $Li_{0.5}Fe_{2.5}O_4$ (0.832 nm) is consistent to values reported by other workers for Ti-substituted $Li_{0.5}Fe_{2.5}O_4$ and reflects nearly equal ionic radii of Ti^{4+} (0.064 nm), Li^{+} (0.068 nm) and Fe^{3+} (0.068 nm) [3,7] .

As a further confirmation that monophasic Ti-substituted $Li_{0.5}Fe_{2.5}O_4$ was prepared by sintering the rutile-containing mixture at 700°C, Fig. 4 shows the Mössbauer spectrum recorded at room temperature from the material. The spectrum was best-fitted with two overlapping sextets corresponding to Fe^{3+} ions on both tetrahedral A- and octahedral B-sites of the lithium spinel ferrite. The hyperfine parameters obtained are summarized in Table 1. The isomer shift, quadrupole and magnetic hyperfine field values for both sextets agree well with those reported for Ti-substituted $Li_{0.5}Fe_{2.5}O_4$ [7,8].

The observed decrease in values of H_{hf} on both sites (Table 1) relative those of pure $Li_{0.5}Fe_{2.5}O_4$ (50.5T and 51.0T for the A- and B- site respectively [7]) is explicable in terms of Neel's molecular field model theory. The substitution of the non-magnetic ions Ti^{4+} and Li^{+} for Fe^{3+} on the B- and A- sites respectively, leads to decreasing the number of Fe^{3+}-O^{2-}-Fe^{3+} magnetic bonds on both sites and consequently their hyperfine field values decrease.

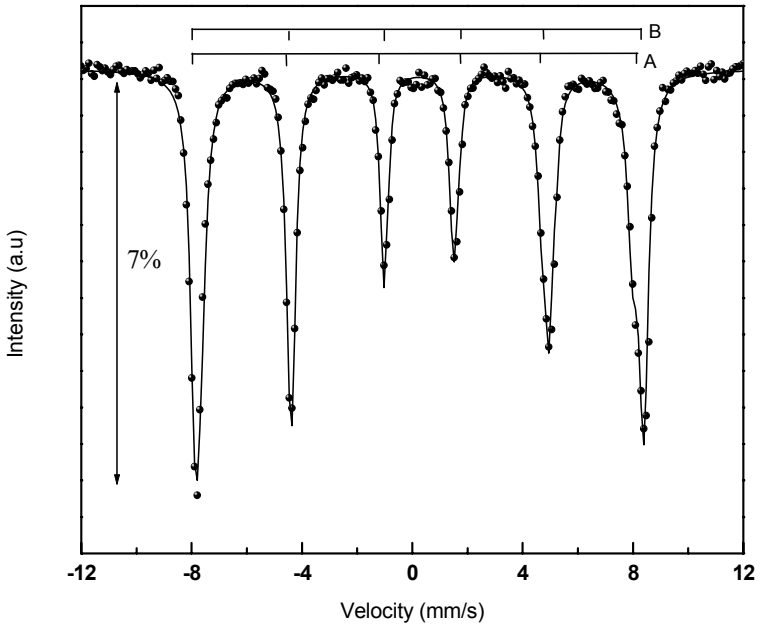

Fig. 4: The room temperature ^{57}Fe Mössbauer spectrum recorded from the 190h-pre-milled mixture of α-Fe_2O_3, the rutile modification of TiO_2 sintered in air at 700°C (12h).

Table 1. Room temperature ^{57}Fe Mössbauer parameters of Ti-substituted $Li_{0.5}Fe_{2.5}O_4$ prepared by sintering the pre-milled rutile-containing mixture at 700°C (see text).

sub-spectrum	IS (mm/s)	QS (mm/s)	H_{hf} (T)	I (%)
A	0.23	0.00	49.2	43
B	0.29	0.00	50.9	57

IS= isomer shift; QS= quadrupole splitting; H_{hf} = hyperfine magnetic field; I = intensity relative to total spectrum.

Taking all Ti^{4+} and excess Li^{+} ions to substitute for Fe^{3+}at the B- and A-sites respectively [6] and assuming a similar recoilless fraction in both sites, the intensities of both sextets (Table 1) suggest for the material obtained at 700°C a compositional formula of $Li_{0.75}Ti_{0.50}Fe_{1.75}O_4$ compared to the initially sought $Li_{0.65}Ti_{0.30}Fe_{2.05}O_4$. While this is not a rigorous way to obtain the composition formula, it nevertheless gives a hint that the amount of Ti^{4+} relative to that of Fe^{3+} in the final product can slightly be larger than initially intended. This may be attributed to α-Fe_2O_3 fine particles that adhere to the walls and the lid of the milling vial during the initial milling stages and hence do not take part in the milling-induced reaction. Consequently this leads to decreasing the Fe^{3+} content in the final product. The discrepancy between the desired composition and the final composition can be minimized by frequently opening the vial and mildly filing the accumulated layer of the reactants on the inner surface of the vial. Of course, the final composition has to be determined using a reliable analytical technique.

We intended the preceding discussion to show that both X-ray diffraction and Mössbauer spectroscopy have shown the material obtained at 700°C by sintering the pre-milled rutile-containing mixture to be single-phased Ti-substituted $Li_{0.5}Fe_{2.5}O_4$. This temperature is *ca.* 450-500°C lower than the temperatures normally used to prepare the material by conventional 'ceramic' double sintering techniques. The efficient sintering in terms of both in the short duration and the low temperature of formation of the final product, achieved here relative to conventional double sintering is obviously a consequent of the prolonged milling process. While short-time milling has been used routinely to produce fine particles with large surface area to facilitate sintering [1,5] in the present work prolonged milling was used to induce a solid state reaction between the initial components as well. Both the fine particles where the initial reactants are tightly pressed and the Li^{+} and/or Ti^{4+}-substituted α-Fe_2O_3 nanoparticles derived from the milling process lead to a large number of ionic diffusion paths that accelerate completion of the reaction using a lower thermal activation energy and hence lower temperature than required conventionally.

3.2.a Milling the anatase-containing mixture

The X-ray powder diffraction patterns recorded from the mixture of α-Fe_2O_3, Li_2CO_3 and the anatase polymorph of TiO_2 following identical milling conditions in air to that used in the case of the rutile-containing mixture are shown in Fig. 5.

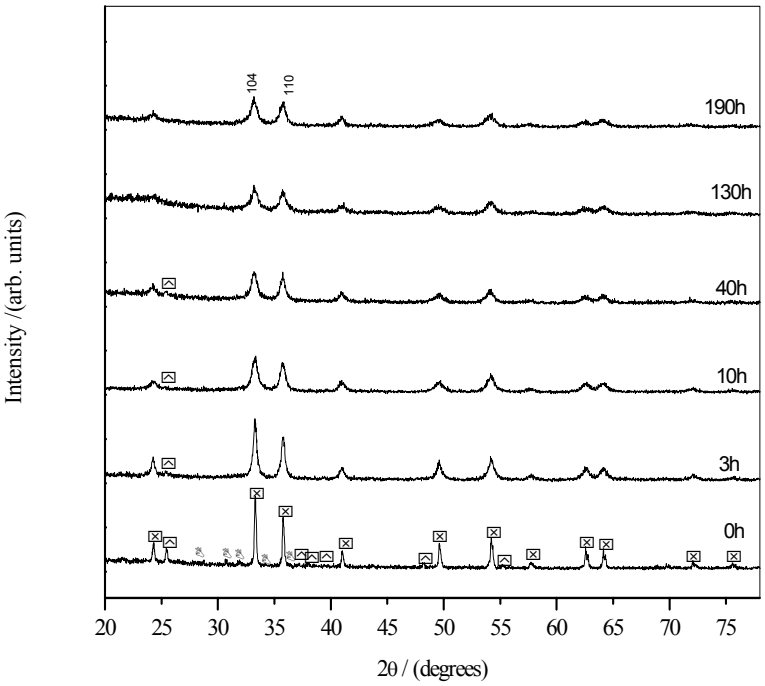

Fig. 5: X-ray powder diffraction patterns recorded from a mixture of α-Fe_2O_3 (ξ), anatase modification of TiO_2 (ψ) and Li_2CO_3 (B) following ball milling at the times indicated. 110 and 104 are the Miller indices of the α-Fe_2O_3 reflection peaks shown.

Generally, as in the case of the rutile-containing mixture, the peaks corresponding to the corundum-related α-Fe_2O_3 progressively broaden and decrease in intensity with increasing milling time up to 190h. The peaks corresponding to Li_2CO_3 completely disappear after 10h of milling, and the relative intensities of the 104 and 110 of α-Fe_2O_3 change in a similar way to that encountered in the case of the rutile-containing mixture. This indicates that milling leads cationic substitution of the α-Fe_2O_3 structure. However, unlike the case of the rutile-containing mixture where the rutile reflection peaks disappear after 3h of milling, the most intense reflection peak of anatase (*ca.* 25.5° 2θ) , can been observed even after 40h of milling. This is indicative that the milling-induced reaction rate between α-Fe_2O_3 with anatase TiO_2 is weaker relative to that with rutile TiO_2. The values of the lattice parameters obtained for the α-Fe_2O_3 related phase following milling the anatase-containing mixture for 190h do reflect that. While the *c* lattice parameters has remained similar to that of pure α-Fe_2O_3, the value of the *a* and *b* parameters were found to be 5.031 Å relative to 5.027Å for the corresponding phase obtained from the rutile-containing mixture. Thus we conclude that less Ti^{4+} and Li^{+} ions are incorporated in the α-Fe_2O_3 structure when anatase was used instead of rutile. To explain that we note that milling pure anatase TiO_2 under identical conditions to those used here converts it after 20h to the rutile form of TiO_2 [17]. However, the anatase-to-rutile conversion mechanism can be precluded in the presence of other phases[17,18]. Since this is applicable to our present case, we conclude that following 190h of milling, the anatase-containing mixture transforms into a mixture of Ti^{4+} and/or Li^{+} substituted α-Fe_2O_3 as well as unreacted α-Fe_2O_3 and anatase particles that did not undergo conversion to rutile.

3.2.b Sintering the pre-milled anatase-containing-mixture

The X-ray powder diffraction patterns recorded from the mixture of α-Fe_2O_3, the anatase polymorph of TiO_2 and Li_2CO_3 milled for 190h following sintering at different temperature for 12-h intervals in air are shown in Fig. 6.

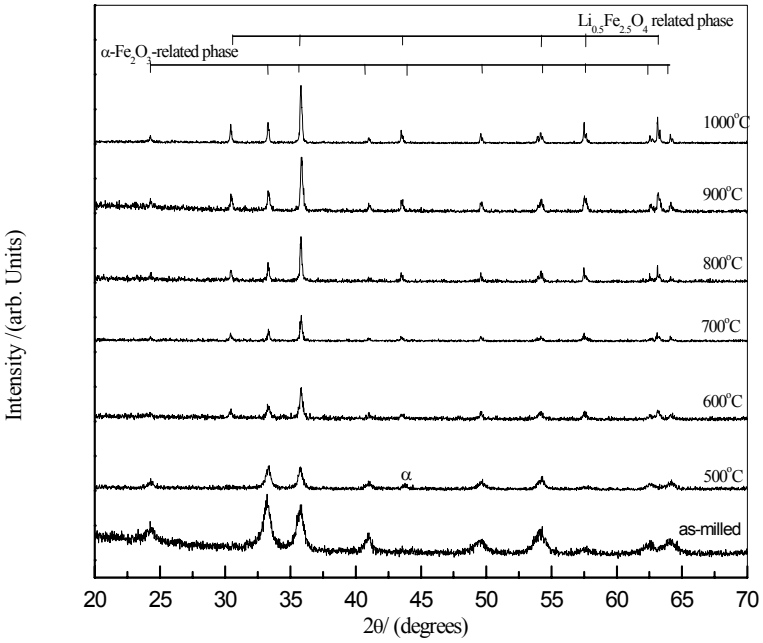

Fig. 6: X-ray powder diffraction patterns recorded from the 190h-pre-milled mixture of α-Fe_2O_3, anatase modification of TiO_2 and Li_2CO_3 following sintering in air for 12-h periods at the temperatures indicated; α refers to α-$LiFeO_2$ related phase.

Sintering the pre-milled anatase-containing mixture at 500°C (12h) followed by quenching in air resulted in the appearance of a broad peak of low intensity centered around *ca.* 43.5° 2θ in the X-ray diffraction (indicated by α in Fig. 6) which may be indexed, as before, to an α-$LiFeO_2$-related phase. The presence of this weak peak (which is the most intense of α-$LiFeO_2$) reflects its small amount as well as the weakness of the induced reaction between the components of the mixture. Comparing this finding with that obtained from the rutile-containing pre-milled mixture sintered at 500°C , viz. the onset of the formation of $Li_{0.5}Fe_{2.5}O_4$ related-phase, indicates that the presence of anatase TiO_2 nanoparticles in pre-milled mixture slows the reaction rate. A simple explanation to that can be the low concentration of both Li^+ and Ti^{4+} in the α-Fe_2O_3 particles relative to those achieved in the case of the rutile-containing mixture. This, in turn, weakens the ionic interdiffusion rates in the anatase-containing mixture.

Sintering the anatase-containing pre-milled mixture at 600°C (12h) followed by quenching in air resulted in the development of a $Li_{0.5}Fe_{2.5}O_4$- related-phase coexisting with unreacted α-Fe_2O_3-related phase. Both phase co-existed as the sintering temperature is increased even up to 1000°C (12h) as seen in Fig. 6.

Thus while it was easy to obtain a monophasic Ti-substituted $Li_{0.5}Fe_{2.5}O_4$ from a pre-milled rutile-containing mixture, the same was not possible when the rutile in the mixture was replaced by the anatase form of TiO_2 using identical milling and sintering regimes. A similar finding was reported by Berry and co-workers [17] who found the formation of monophasic pervoskite-related $CaTiO_3$ to be more easily achieved by milling CaO with the rutile modification of TiO_2 than with the anatine form. The arguments given in the present work can be equally valid in that case.

4. Conclusion

Sintering a 190h pre-milled mixture of Li_2CO_3, α-Fe_2O_3 and the rutile polymorph TiO_2 led to the formation of a single-phase spinel-related Ti-substituted $Li_{0.5}Fe_{2.5}O_4$ at 700ºC (12h). X-ray diffraction and Mössbauer techniques confirm the similarity of the structural and hyperfine parameters of the resulting material to those of Ti-substituted $Li_{0.5}Fe_{2.5}O_4$ prepared using other routes. The lowering in the formation temperature is a consequence of both particle size a milling-induced reaction that led to the diffusion of Li^+ and Ti^+ as substitute cations in the α-Fe_2O_3 structure resulting in a large number of number of ionic diffusion paths that accelerate the reaction. Formation of monophasic Ti-substituted $Li_{0.5}Fe_{2.5}O_4$ was not possible using a similar pre-milled mixture containing anatase rather than rutile TiO_2 even after sintering at 1000^{o}C (12h). This is related to the resistance of anatase to convert to rutile when milled in the presence of other phases

Acknowledgments

This work was done within the framework of the Associateship Scheme of the Abdus Salam International Centre for Theoretical Physics, Trieste, Italy. Financial support from the Swedish International Development Cooperation Agency is acknowledged. X.R. thanks the China Scholarship Council for financial support. The authors are grateful to Professor F.J. Berry for helpful discussions.

References

1. P.D. BABA, G.M. ARGENTINA, *IEEE Trans. Microwave Theory Technol*. 22(1974)654.
2. F. DES. BARROS, P.J. VICCARD and J.O. ARTMAN, *Phys. Lett. A*. 27(1968)374.
3. H.M. WIDATALLAH, C, JOHNSON, F.J. BERRY, M. PEKALA, *Solid State Coummun.* 120 (2001)171.
4. H.M. WIDATALLAH, F.J. BERRY, *J. Solid. State Chem.* 164(2002)230.
5. S. SCHARNER, W. WEPPNER, P. SCHIM-BEURMANN, *J. Solid. State Chem.* 134(1997)170.
6. H.M. WIDATALLAH, E.A. MOORE, *J. Phys. Chem. Solids* 65(2004)1663.
7. A.A. YOUSIF, M.E. ElZAIN, S.A. MAZEN, H.H. SUTHERLAND, M.H. ABDALLAH, S.F. MANSOUR, *J. Phys.: Condens. Matter* 6(1994)5717.
8. P. KISHAN, C. PRAKASH, J.S. BAIJAL, K.K. LAROIA, *Phys. Stat. Sol. (A)* 84(1984)35.
9. R.A. McCURRIE in "Ferromagnetic Materials Structure and Properties" (Academic Press, San Diego, 1994) p. 123.
10. A. CRUSKOVA, J. LIPKA, J. SLAMA, I. TOTH, M. SEBERINI, *Phsy. Stat. Solid A*, 122(1990) K171.
11. V. SEPELAK, *Ann. Chim Sci. Mat.* 27(2002)61.
12. J.S. JIANG, L. GAO, J.K. GUO, X.L. YANG, H.I. SHEN, *J. Inorg. Mater. (China)* 14(1999)390.
13. W. KRAUS, G. NOLZE, *J. Appl. Cryst.* 29(1996)301.
14. F.J. BERRY, C. GREAVES, J. McMANUS, M. MORTIMER, G. OATES, *J. Solid State Chem.* 130(1997) 272.
15. F.J. BERRY, J. F.MARCO, S.J. STEWART, H.M. WIDATALLAH, *Solid State Commun.* 117(2001)235.
16. M. TABUCHI, K. ADO, H. SAKAEBE, C. MASQUELIER, H. KAGEYAMA, O. NAKAMURA, *Solid State Ionics* 79(1995)220.
17. F.J. BERRY, P. WYNN, J.Z. JIANG, S. MØRUP, *J. Mater. Sci.* 36(2001)3637.
18. S. RIYAS, V. AHMED YASIR, P.N. MOHAN DAS, *Bull. Mater. Sci*. 25(2002)267.